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(54) **Aliphatic polyester composition and flexible products**

(57) The present invention relates to biodegradable plastics and biodegradable plastic products thereof having flexibility, and more specifically, it aims to provide a plasticizer for providing aliphatic polyester, in particular, polylactic acid with flexibility, an aliphatic polyester composition using the same, a film, a sheet, a bag and the like obtained by molding said composition, that are, with respect to 100 parts by weight of aliphatic polyester, (1) an aliphatic polyester compound which contains polyg-

lycerol acetic ester by 5-50 parts by weight, (2) an aliphatic polyester compound which contains polyglycerol acetic ester and acetic and fatty acid ester of glycerol having a specific structure by 5-50 parts by weight, and (3) flexible products which are obtained by molding the fatty polyester compound indicated in the above (1) or (2) into films, sheets, bags or the like.

Description

[0001] The present invention relates to plastics, especially biodegradable plastics, and products thereof; most preferably, it relates to a biodegradable aliphatic polyester composition and flexible moldings, which are prepared by blending aliphatic polyester containing polylactic acid as its major constituent with a plasticizer having a specific structure.

Description of the prior art:

[0002] Plastic products of polyethylene, polystyrene, polypropylene, polyvinyl chloride and the like have been utilized in various and wide fields of food packaging, building materials, home electrical appliances and the like and have become indispensable in daily life.

[0003] However, while on one hand such plastic products have a feature of durability, they also have disadvantages in causing destruction to the environment, such that when they have fulfilled their utilizing purpose and have become waste, they show poor degradability in nature because of their superior durability and affect the biological system.

[0004] For overcoming such disadvantages of plastics, biodegradable plastics have received considerable attention. Biodegradable plastics are degraded into low molecular weight compounds in an extremely short time by enzymatic actions produced by microorganisms which inhabit the environment, and is finally degraded into inorganic substances such as water and carbon dioxide.

[0005] With the growing awareness of environmental problems in recent years, recycling of plastic products has been legislated, and along with recycling and reuse thereof, the so-called biodegradable plastics, which can be easily degraded in the environment, have received considerable attention and both governments and the private sector have keenly carried out research and development thereof. As uses thereof, application to agricultural materials (such as, for example, sheets or films to be used for greenhouses for growing root vegetables) to be used in the environment, materials (such as, for example, food package films, sheets, or bags) to be used in the food packaging field where collection is difficult and, other packaging materials (such as, for example, sheets, films, or bags for packaging clothes or convenience goods), etc., has been anticipated.

[0006] Such biodegradable plastics can be divided into some large groups such as microorganism-producing system, natural substance-utilizing system, and chemically synthesized system, and wherein aliphatic polyester system, denatured polyvinyl alcohol system, denatured starch system, and other system are now on first steps for practical use.

[0007] Polybutylene succinate, polyhydroxybutyrate and the like can be used as for aliphatic polyester plastics, and polylactic acid can be used as for a semi-synthetic copolymer.

[0008] Polylactic acid is a crystalline thermoplastic macromolecular having tensile strength equivalent to that of polyethylene and transparency equivalent to that of polyethylene terephthalate, is used in medical suture threads and the like, is highly safe and, when burned, the small combustion calorie which is approximately 1/3 of that of polyethylene, polypropylene or the like causes less damage to an incinerator, and generates no poisonous gas. Moreover, with these advantages, in recent years, research and development of manufacturing methods, application, uses and the like have become active, therefore, diversification of uses and an accompanying increase in production are expected in the future.

[0009] Polylactic acid has such advantages, however, on the other hand, wherein plastic products thereof are hard and the utilization has been restricted in fields which require softness and, particularly, in films, package materials and the like. The addition of a plasticizer is one of method for improving hardness and providing softness, and for actions as a plasticizer, conditions such as:

(1) being excellent in compatibility with a polymer or a resin to be plasticized,

(2) having good plasticizing efficiency, and

(3) showing no deterioration in performance due to volatilization, transition, or oozing after processing, must be provided.

[0010] As a plasticizer for containing polylactic acid and a resin containing polylactic acid as its major constituent, triacetin (Shimazu Hyoron, Vol.54, No. 155 (1997. 3): Japanese Unexamined Patent Publication No. Hei-6-184147: Japanese Unexamined Patent Publication No. Hei-7-177826), ester of aliphatic dicarboxylic acid and/or chain molecular diol or an aliphatic polyester containing these as its major constituents (Japanese Unexamined Patent Publication No. Hei-8-199053: Japanese Unexamined Patent Publication No. Hei-8-245866), triacetin, tributyn, or butylphthalyl butylglycolate (Japanese Unexamined Patent Publication No. Hei-9-296103), a glycerol derivative including an alkyl group having carbon numbers 1-10 (Japanese Unexamined Patent Publication No. Hei-11-323113), diacetyl monoacyl glycerol including an acyl group having carbon numbers 6-18 (Japanese Unexamined Patent Publication No. 2000-302956) and the like have been disclosed. However, each of these has advantages and disadvantages in performance and physical characteristics and is not sufficiently satisfactory.

[0011] Preferred embodiments of the present invention may provide a plasticizer for providing aliphatic polyester, in

particular, polyactic acid with flexibility, an aliphatic polyester composition using the same and flexible moldings which are obtained by molding said composition into films, sheets, bags and the like.

[0012] The present inventors have repeatedly carried out intensive research studies and consequently discovered that good results can be achieved by blending aliphatic polyester with a specific compound as a plasticizer. Based on this knowledge, the present invention has been reached.

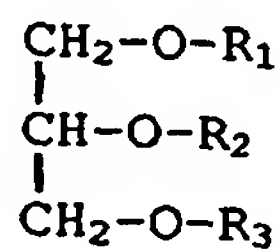
[0013] The present invention has the following constructions.

1. An aliphatic polyester composition which contains, with respect to 100 parts by weight of aliphatic polyester, polyglycerol acetic ester by 5-50 parts by weight.

2. An aliphatic polyester composition which contains, with respect to 100 parts by weight of aliphatic polyester, polyglycerol acetic ester and a compound represented by the following general formula (1) by 5-50 parts by weight.

General formula (1)

[0014]



[0015] (In the formula, at least one of R_1 , R_2 , and R_3 is an acyl group having carbon numbers 8-22 and the rest thereof are acetyl groups or hydrogen atoms.

3. An aliphatic polyester composition as set forth in Claim 2, wherein in the general formula (1), at least one of R_1 , R_2 , and R_3 is an acyl group having carbon numbers 8-18 and the rest thereof are acetyl groups.

4. An aliphatic polyester composition as set forth in the above 2, wherein the compound represented by the general formula (1) is at least one selected from glycerol diacetomonoacprate, glycerol diacetomonoaurate, and glycerol diacetomonooleate.

5. An aliphatic polyester composition as set forth in any of the above 1-4, wherein the polymerization degree of polyglycerol as a component of polyglycerol acetic ester is 2-4.

6. An aliphatic polyester composition as set forth in any of the above 1-5, wherein the acetylation degree of polyglycerol acetic ester is 50-100%.

7. An aliphatic polyester composition as set forth in any of the above 1-6, wherein the polyglycerol acetic ester is at least one or a mixture of two or more selected from diglycerol diacetate, diglycerol triacetate, and diglycerol tetraacetate.

8. An aliphatic polyester composition in which the aliphatic polyester as set forth in any of the above 1-7 is polylactic acid.

9. Flexible products which are obtained by molding the aliphatic polyester composition as set forth in any of the above 1-8 into films, sheets, bags or the like.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0016] The present invention will be described in further detail.

[0017] The polyester in the present invention mainly deals with polylactic acid. A polylactic resin of any degree of polymerization or quality can be used. Not only a homopolymer of polylactic acid, but also a copolymer of glycolic acid, s-caprolactone, trimethylene carbonate, polyethylene glycol or the like may be concomitantly used. In addition, to the extent where the physical characteristics of the polylactic resin are not lost, another biodegradable macromolecule such as cellulose acetate, polycaprolactone, polybutylene succinate, a polyhydroxybutyrate-valerate copolymer, chitin, chitosan, or starch may be blended.

[0018] Polyglycerol acetic ester is used as a main plasticizer in the present invention. Herein, as polyglycerol, glycerol having an average polymerization degree of 2-12 can be mentioned, which is preferably, 2-6, and more preferably, 2-4. Concretely, diglycerol, triglycerol, tetraglycerol, pentaglycerol, hexaglycerol and the like can be exemplified, and these can be used alone or as a mixture with an arbitrary combination.

[0019] The preparation of polyglycerol acetic ester is not particularly limited, however, for example, a method where

acetic anhydride is used, an esterification reaction using acetic acid and the like can be mentioned. The esterification degree of acetic acid with respect to a hydroxyl group of polyglycerol (hereinafter, abbreviated as an "acetylation ratio") is preferably 50% or more, and more preferably, 75-100%.

[0020] The acetylation ratio of polyglycerol acetic ester is calculated by the following formula.

[Numerical formula 1]

[0021]

$$\text{Acetylation ratio} = \frac{\text{Ester value}}{\text{Ester value} + \text{Hydroxyl group value}} \times$$

100

Formula (1)

[0022] Herein, Ester value = Saponification value - Acid value

[0023] In the present invention, polyglycerol acetic ester and glycerol acetic fatty ester expressed by the above general formula (1) may be concomitantly used as a plasticizer. In this case, the ratio of polyglycerol acetic ester is preferably 10 weight percent or more in the mixture of both.

[0024] An acetyl group of the glycerol acetic fatty ester used herein is 2 mol or less on average with respect to 1 mol-glycerol. An acyl group having carbon numbers 8-22 (hereinafter, referred to as an "acyl group of C8-22"), preferably, having an acyl group of C8-18 is 1 mol or more on average with respect to 1 mol-glycerol. In addition, in consideration of compatibility between this compound and aliphatic polyester, the hydroxyl group value of this compound is preferably 20 or less. In addition, the state of this compound is preferably liquid at room temperature for workability.

[0025] In the general formula (1), ester where at least one of R_1 , R_2 , and R_3 is an acyl group of C8-22 and the rest thereof are acetyl groups is further preferable. As particularly preferable compounds, glycerol diacetomonocapirate, glycerol diacetomonolaurate, and glycerol diacetomonooleate can be mentioned, and these can be used alone or in a mixed fashion. As commercial products of glycerol diacetomonolaurate, RIKEMAL PL-004, PL-012, and PL-014 [manufactured by Riken Vitamin Co., Ltd., trade names] can be mentioned, and as commercial products of glycerol diacetomonooleate, POEM G-038 and POEM G-048 [manufactured by Riken Vitamin Co., Ltd., trade names] can be mentioned.

[0026] The amount of these plasticizers to be added influences the finished products in terms of the degree of crystallization, flexibility, heat resistance and the like. If the amount to be added is too great, the degree of crystallization and heat resistance decline, whereas if it is too small, sufficient flexibility cannot be obtained. Based on such a viewpoint, the amount of the plasticizers to be added is preferably 5-50 parts by weight with respect to 100 parts by weight of aliphatic polyester, and more preferably, 10-30 parts by weight.

[0027] To an aliphatic polyester composition according to the present invention, in addition to the aliphatic polyester as the major constituent and the plasticizer of the present invention (a polyglycerol acetic ester alone or a mixture of this polyglycerol acetic ester and a compound expressed by the above general formula (1)), to the extent where the object of the present invention is not lost, additives such as an anti-blocking agent, a lubricant, an antistatic agent, an anticlouding agent, a ultraviolet absorbing agent, a heat stabilizer, an antioxidant, a color protector, a filler, a pigment, a flame retardant and the like may be added according to use. As these additives, widely known additives can be used without particular restriction.

[0028] For the aliphatic polyester composition according to the present invention, a method where, after aliphatic polyester, a plasticizer of the present invention, and, in some cases, other additives are mixed to become uniform by means of a high-speed or low-speed stirrer, the mixture is melted and kneaded by means of a single screw or multi-screw extruder having a sufficient kneading ability can be employed. The shape of an aliphatic polyester composition (a resin composition) according to the present invention is preferably pellets, a stick shape, powder and the like.

[0029] The aliphatic polyester composition (resin composition) obtained as in the above is molded into a film shape or a sheet shape by a hot extrusion method using an extruder fitted with a T-die. In addition hereto, manufacturing can also be carried out by a hot extrusion method using an extruder fitted with a circular die, that is, by an inflation molding method.

[0030] The drawn film or sheet obtained by the above method may be cut into an appointed size and used as a cut sheet, or the drawn film may be formed into a bag shape and used. As a method for forming a bag, a heat sealing method, a high-frequency method and the like can be mentioned.

[0031] Objects to be packaged by these drawn films or sheets are not particularly limited. In general, food, medical supplies, cosmetics, fertilizers, electric appliances, paper products, and refuse thereof, etc., can be mentioned. Preferably, foods such as vegetables, fruits, seafood, meat, grain, dried foodstuffs, bread, dairy products, noodles, sweets, confectionery, wild plants, and seasonings and refuse thereof, etc., can be mentioned.

[0032] As concrete examples for use as bags, food bags, shopping bags, disposal bags, compost bags, and sandbag sacks, etc., can be mentioned. As concrete examples for use as cut sheets, wrapping films for food packages, wrapping films for cosmetics, wrapping films for medical supplies, wrapping films for surgical liniment, wrapping films for agriculture, and wrapping films for electric appliances, etc., can be mentioned. In addition, drawn films or sheets can be used as flexible moldings such as agricultural films for horticultural facilities and the like, base material films for adhesive tapes, and waterproof sheets.

EMBODIMENT

[0033] Hereinafter, the present invention will be described concretely by means of an embodiment.

[Test sample]

[0034]

- <Sample 1> Diglycerol acetic ester (Acetylation ratio: 50%)
- <Sample 2> Diglycerol acetic ester (Acetylation ratio: 75%)
- <Sample 3> Diglycerol acetic ester (Acetylation ratio: 100%)
- <Sample 4> Triglycerol acetic ester (Acetylation ratio: 100%)
- <Sample 5> Tetraglycerol acetic ester (Acetylation ratio: 100%)
- <Sample 6> Hexaglycerol acetic ester (Acetylation ratio: 100%)
- <Sample 7> Decaglycerol acetic ester (Acetylation ratio: 100%)
- <Sample 8> Diglycerol acetic ester (Acetylation ratio: 100%)/Glycerol diacetomonocapirate = 1:9
- <Sample 9> Diglycerol acetic ester (Acetylation ratio: 100%)/Glycerol diacetomonocapirate = 1:1
- <Sample 10> Diglycerol acetic ester (Acetylation ratio: 100%)/Glycerol diacetomonocapirate = 3:1
- <Sample 11> Diglycerol acetic ester (Acetylation ratio: 100%)/Glycerol diacetomonolaurate = 1:1 <Trade name: RIKEMAL PL-012, manufactured by Riken Vitamin Co.,Ltd.>
- <Sample 12> Diglycerol acetic ester (Acetylation ratio: 100%)/Glycerol diacetomonooleate = 1:1 <Trade name: POEM G-038, manufactured by Riken Vitamin Co.,Ltd.>
- <Sample 13> Diglycerol acetic ester (Acetylation ratio: 100%)/Glycerol diaceto monoerucin = 1:1
- <Sample 14> Diglycerol acetic ester (Acetylation ratio: 100%)/Glycerol monoaceto dilaurate = 1:1
- <Sample 15> Di(2-ethylhexyl) phthalate <Commercially available product>
- <Sample 16> Dibutyl phthalate <Commercially available product>
- <Sample 17> Acetyl tributyl citrate <Commercially available product>
- <Sample 18> Glycerol triacetate <Commercially available product>

[Preparation example 1]

[0035] Polylactic acid [Trade name: Polylactic acid Lacty #9021 (Average molecular weight: 145,000) manufactured by Shimadzu Corporation] was heated at 110°C for 4 hours for elimination of moisture contained therein. Then, a prescribed amount of plasticizer was added to 100 parts by weight of the dry polylactic acid thus obtained and mixed to become uniform by means of a high-speed stirrer. Thereafter, the mixture was melted and kneaded by means of a twin screw extruder and extruded at 200°C, whereby pellets were fabricated.

[Test example 1] Tensile test (Conforms with JIS K-7113)

[0036] In terms of the respective pellets obtained in Preparation example 1, first test pieces were fabricated by means of an injection molding machine (IS55EPN, manufactured by Toshiba Machine Co., Ltd.), and the pieces, after preservation for a day under conditions wherein the temperature was 23°C and the relative humidity was 50%, were supplied for testing. A Tensilon universal-testing machine (RTC-1310, manufactured by Orientech Inc.) was used as a testing instrument, and a test was performed under conditions wherein the chuck interval was 120mm and the test rate was 200mm/minute.

[Test example 2] Bending test (Conforms with JIS K-7203)

[0037] In terms of the respective pellets obtained in Preparation example 1, test pieces having a thickness of 6mm, a width of 10mm, and a length of 12cm were fabricated by means of an injection molding machine (IS55EPN, manufactured by Toshiba Machine Co., Ltd.), and the pieces, after preservation for a day under conditions wherein the

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temperature was 23°C and the relative humidity was 50%, were supplied for testing. A Tensilon universal-testing machine (RTC-1310, manufactured by Orientech Inc.) was used as a testing instrument, and a test was performed under a condition wherein the test rate was 3mm/minute.

5 [Test example 3] Bleeding

[0038] In terms of the respective pellets obtained in Preparation example 1, test pieces having a thickness of 3mm, a width of 10mm, a length of 10mm were fabricated by means of an injection molding machine (IS55EPN, manufactured by Toshiba Machine Co., Ltd.) and preserved for a week under conditions wherein the temperature was 50°C and the relative humidity was 50%, and then the degree of bleeding was observed.

[0039] The results of the above tests are shown in Tables 1-5. Herein, the "part" in the tables represents parts by weight.

[Table 1]

	Example	Example 1 2	Example 3
Plasticizer sample	Sample 3	Sample 3	Sample 3
Blending amount (part)	5	20	50
Maximum tensile stress (Mpa)	66.2	17.2	7.2
Modulus of elasticity in tension (Mpa)	935.1	56.9	26.7
Maximum bending stress (Mpa)	39.2	14.8	5.9
Modulus of elasticity in bending (Mpa)	367.2	44.5	24.9
Bleeding	None	None	None

[Table 2]

	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Plasticizer sample	Sample 4	Sample 5	Sample 6	Sample 7	Sample 1	Sample 2
Blending amount (part)	20	20	20	20	20	20
Maximum tensile stress (Mpa)	17.3	18.4	21.2	23.5	19.2	18.5
Modulus of elasticity in tension (Mpa)	58.5	60.1	88.7	102.2	61.4	58.7
Maximum bending stress (Mpa)	16.3	17.8	20.9	24.8	17.8	15.1
Modulus of elasticity in bending (Mpa)	45.4	46.9	67.6	91.3	47.3	46.3
Bleeding	None	None	Slightly	Somewhat significant	None	None

[Table 3]

	Example 10	Example 11	Example 12
Plasticizer sample	Sample 9	Sample 9	Sample 9
Blending amount (part)	5	20	50
Maximum tensile stress (Mpa)	72.8	18.9	7.9
Modulus of elasticity in tension (Mpa)	1028.6	62.6	29.4
Maximum bending stress (Mpa)	43.1	16.3	6.5

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[Table 3] (continued)

	Example 10	Example 11	Example 12
Plasticizer sample	Sample 9	Sample 9	Sample 9
Modulus of elasticity in bending (Mpa)	403.9	48.9	27.4
Bleeding	None	None	None

[Table 4]

	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
Plasticizer sample	Sample 11	Sample 12	Sample 13	Sample 14	Sample 8	Sample 10
Blending amount (part)	20	20	20	20	20	20
Maximum tensile stress (Mpa)	19.0	20.2	23.3	25.9	15.6	18.2
Modulus of elasticity in tension (Mpa)	64.4	66.1	195.2	449.6	56.4	57.0
Maximum bending stress (Mpa)	17.9	19.6	23.0	27.3	14.4	15.1
Modulus of elasticity in bending (Mpa)	49.9	51.6	148.8	401.6	44.5	46.1
Bleeding	None	None	Slightly	Somewhat significant	Slightly	None

[Table 5]

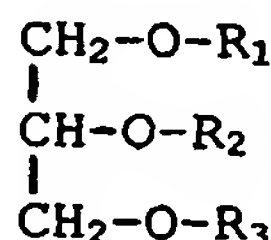
	Comparative example 1	Comparative example 2	Comparative example 3	Comparative example 4	Comparative example 5
Plasticizer sample	Sample 15	Sample 16	Sample 17	Sample 18	None
Blending amount (part)	20	20	20	20	
Maximum tensile stress (Mpa)	55.1	45.7	42.1	38.4	81.4
Modulus of elasticity in tension (Mpa)	1264.7	1086.2	926.7	889.4	2552.3
Maximum bending stress (Mpa)	47.8	926.7	40.5	34.6	100.7
Modulus of elasticity in bending (Mpa)	1099.2	889.4	869.3	786.2	2707.0
Bleeding	Signifi-cant	Signifi-cant	Signifi-cant	None	None

[0040] According to the present invention, flexibility is provided for the aliphatic polyester composition containing polylactic acid or a lactic unit, as a result, the aliphatic polyester compositions can be satisfactorily used as flexible moldings such as packaging films for food, medical supplies, and cosmetics, etc., films for agriculture, films for engineering and construction and the like, and as extensive materials. In particular, in collection of municipal refuse, by separately collecting refuse such as scraps of vegetables with the bags of the present invention, not only does incineration but disposal by composting the garbage also become possible.

Claims

1. An aliphatic polyester composition which contains, with respect to 100 parts by weight of aliphatic polyester, polyglycerol acetic ester by 5-50 parts by weight.
2. An aliphatic polyester composition which contains, with respect to 100 parts by weight of aliphatic polyester, polyglycerol acetic ester and a compound represented by the following general formula (1) by 5-50 parts by weight:

General formula (1)



wherein at least one of R_1 , R_2 and R_3 is an acyl group having carbon numbers 8-22 and the rest thereof are acetyl groups or hydrogen atoms.

3. An aliphatic polyester composition as set forth in Claim 2, wherein in the general formula (1), at least one of R_1 , R_2 , and R_3 is an acyl group having carbon numbers 8-18 and the rest thereof are acetyl groups.
4. An aliphatic polyester composition as set forth in the above 2, wherein the compound represented by the general formula (1) is at least one selected from glycerol diacetomonoacprate, glycerol diacetomonolaurate, and glycerol diacetomonooleate.
5. An aliphatic polyester composition as set forth in any of the above 1-4, wherein the polymerization degree of polyglycerol as a component of polyglycerol acetic ester is 2-4.
6. An aliphatic polyester composition as set forth in any of the above 1-5, wherein the acetylation degree of polyglycerol acetic ester is 50-100%.
7. An aliphatic polyester composition as set forth in any of the above 1-6, wherein the polyglycerol acetic ester is at least one or a mixture of two or more selected from diglycerol diacetate, diglycerol triacetate, and diglycerol tetraacetate.
8. An aliphatic polyester composition in which the aliphatic polyester as set forth in any of the above 1-7 is polylactic acid.
9. Flexible products which are obtained by molding the aliphatic polyester composition as set forth in any of the above 1-8 into films, sheets, bags or the like.

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EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IntCl.7)
Y	EP 1 029 890 A (MITSUI CHEMICALS INC) 23 August 2000 (2000-08-23) *Abstract* *Tables* * paragraphs [0007] - [0009], [0015], [0016], [0024], [0025], [0038], [0048]; claims 1-10 *	1-9	C08K5/103 C08K5/00 C08L67/00 C08L67/02 C08L67/04
Y	GB 364 807 A (BOEHRINGER & SOEHNE GMBH) 14 January 1932 (1932-01-14) * column 1, line 19 - column 3, line 8; claims 2-4 *	1-9	
A	US 5 500 465 A (KRISHNAN MOHAN ET AL) 19 March 1996 (1996-03-19) * column 3, line 45 - line 50 * * column 4, line 15 - line 33 * * column 5, line 42 - line 48 * * column 8, line 4 - line 11 * * column 9, line 58 - column 10, line 13; claims 23,27,28 * * column 6, line 26 - line 40 *	1-9	
A	US 5 753 782 A (HAMMOND TIMOTHY ET AL) 19 May 1998 (1998-05-19) * column 1, line 3 - line 5 * * column 1, line 60 - column 2, line 2 * * column 5, line 16 - line 17 * * column 6, line 30 - line 43; claim 8 *	1-9	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IntCl.7)
Place of search MUNICH		Date of completion of the search 22 October 2002	Examiner Zeslawski, W
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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22-10-2002

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1029890	A	23-08-2000	EP 1029890 A2	23-08-2000
			JP 2000302956 A	31-10-2000
GB 364807	A	14-01-1932	NONE	
US 5500465	A	19-03-1996	AT 219783 T	15-07-2002
			CA 2183772 A1	14-09-1995
			DE 69527191 D1	01-08-2002
			EP 0749460 A1	27-12-1996
			JP 2813470 B2	22-10-1998
			JP 9505107 T	20-05-1997
			WO 9524447 A1	14-09-1995
US 5753782	A	19-05-1998	AU 6851694 A	20-12-1994
			CA 2163444 A1	08-12-1994
			EP 0701586 A1	20-03-1996
			WO 9428061 A1	08-12-1994
			JP 9501450 T	10-02-1997

EPO FORM P0459

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